

PATENT SPECIFICATION

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NO DRAWINGS

- (21) Application No. 6372/70 (22) Filed 10 Feb. 1970
(31) Convention Application No. 812 407 (32) Filed 1 April 1969 in
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(72) Inventors ORVILLE DEACY FRAMPTON and JULIAN FELDMAN



(54) IMPROVED ALCOHOL CATALYST AND PROCESS

(71) We, NATIONAL DISTILLERS AND CHEMICAL CORPORATION of 99 iron and aluminium phosphates dissolved in phosphoric acid tends to "weep" from the ca-

PATENTS ACT 1949

SPECIFICATION NO 1306141

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 12 July 1978 this Specification has been amended under Section 33 in the following manner:

Page 1, line 74, *delete* having a pore volume

Page 1, *delete* lines 75 and 76

Page 1, line 81, *delete* preferred support *insert* support used according to the invention

Page 5, line 32, *delete* 2.2 *insert* 1.2

Page 5, line 33, *delete* 200 to 600 *insert* 300 to 400

Page 5, *delete* lines 36 to 39

Page 5, *for* Claims 3 to 9 *read* Claims 2 to 8

Page 5, line 40, *delete* or 2

Page 5, line 43, *delete* 1, 2 or 3 *insert* 1 or 2

Page 5, line 45, *for* 4 *read* 3

Page 5, line 51, *delete* 4 or 5 *insert* 3 or 4

Page 5, line 54, *delete* 4, 5 or 6 *insert* 3, 4 or 5

Page 5, line 61, *for* 8 *read* 7

THE PATENT OFFICE
25 October 1978

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SPECIFICATION AMENDED - SEE ATTACHED SLIP

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 (72) Inventors ORVILLE DEACY FRAMPTON and JULIAN FELDMAN



(54) IMPROVED ALCOHOL CATALYST AND PROCESS

- (71) We, NATIONAL DISTILLERS AND CHEMICAL CORPORATION of 99 Park Avenue, New York, New York, United States of America, a corporation organised and existing under the laws of the State of Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates generally to a process for the hydration of olefins to alcohols and other products.
- It is well known that olefins may be directly hydrated to the corresponding alcohols (e.g. ethylene to ethanol) by continuously passing a gaseous mixture of the olefin and water vapour at elevated temperature and pressure through a catalyst bed comprising a solid porous siliceous support which is incompletely saturated with an aqueous solution of phosphoric acid. Further amounts of an aqueous solution of free phosphoric acid are added to the bed during the process to make up for the losses of phosphoric acid from the bed and to maintain the activity of the latter at a high level. For the hydration of ethylene to ethanol reaction temperatures in the vicinity of 300°C are preferred, and the various conditions of temperature, pressure and ratio of ethylene to water vapour in the feed are adjusted so as to bring the acid in the bed to a concentration sufficient to maintain the activity of the catalyst high enough to produce ethanol.
- Siliceous material was selected as support because it is relatively inert to phosphoric acid under hydration conditions. The many such supports which have been disclosed may be divided into three classes: diatomaceous earths, synthetic silica, and clays such as bentonite or Fullers earth which are aluminium silicates. The importance of removing iron and aluminium oxide and/or silicates has been recognised. Semi-liquid material consisting of iron and aluminium phosphates dissolved in phosphoric acid tends to "weep" from the catalyst causing plugging and other harmful effects. Iron oxide tends to promote cracking of the olefin undergoing hydration. Acid leach of some of the aluminium silicate clay supports has been reported as lowering aluminium content. However, in many cases removal of these undesirable impurities has not been sufficiently complete.
- The catalyst support which has been preferred for use comprises a calcined diatomaceous earth. A particular useful calcined diatomaceous earth product which was found is that manufactured by the Johns-Manville Corporation and marketed under the trade name "Celite" (Registered Trade Mark).
- The present invention is concerned with the use of silica gels as the catalyst support. In the following description and claims, all parts and percentages are by weight unless otherwise specified.
- The present invention provides a process for the preparation of alkanol by olefin hydration which comprises reacting a gaseous mixture of an olefin and water at elevated temperature and pressure in the presence of an olefin hydration catalyst which comprises a solid, porous silica gel support having a pore volume of from 1 to 2.2 cc per gram and a surface area from 200 to 600 square metres per gram, impregnated with phosphoric acid. The silica gel used is preferably of high purity, being low in content of impurities such as aluminium and iron, as well as other contaminants including sodium oxide. The preferred support has a pore volume of from 1 to 1.2 cc/gm and a surface area of from 300 to 400 m²/gm.
- The following comparison of properties serves to show differences in surface properties among diatomaceous earth, Celite VIII, acid leached Celite VIII, acid leached bentonite, and a preferred low density silica gel support employed according to the invention.

[Price 25p]

Support	Average Pore Radius Å	Pore Volume cc/gm	Surface Area sq.m/gm
Preferred silica gel	70	1.16	325
Celite VIII (Diatomaceous earth)	—	0.56	3—10
Leached Celite VIII as in U.S. Patent 2,960,477	200—6500	0.6 to 1.1	5—20
Leached bentonite as in German Patent 1,156,772	—	0.72 to 0.80	—

5 The silica gel support employed in this invention may be selected from a commercially available source or prepared by known methods found in the following references: C. J. Plank and L. C. Drake, *Journal of Colloid Science*, 2, 399—412 (1947); Ralph K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, New York (1955); and James C. Vail, *Soluble Silicates, Their Properties and Uses*, Volumes I and II, Reinhold Publishing Corporation, New York (1952).

10 The pore diameter, which may be calculated by known methods from the two parameters, surface area and pore volume, may be a significant factor in the activity of the catalyst. Another significant factor in catalyst activity may be the pore size distribution characteristic of low density silica gels, e.g. a relatively low proportion of micropores as indicated by a low nitrogen adsorption at low values of P/P_0 , and high adsorption at values of P/P_0 near unity, where P and P_0 represent the equilibrium pressure of nitrogen vapour (at the boiling point of liquid nitrogen) over the gel and saturation vapour pressure of liquid nitrogen respectively.

15 The chemical composition of the support, in terms of weight percent on dry basis, generally comprises at least 99.0% SiO_2 ; FeO , at most 0.03%, e.g. 0.01 to 0.03%; Na_2O at most 0.1%, e.g. 0.02 to 0.09%; and Al_2O_3 at most 0.5%, e.g. less than 0.4%. One gel suitable for use according to the invention has the following specific properties:

pore volume, 1.16 cc/g; surface area, 325 sq. m/g; average pore diameter, 140Å; bulk density, about 27 lbs/cu. ft. Good mechanical stability on exposure to high temperature steam, e.g. at temperatures up to 320°C, preferably at 300 to 320°C, is a preferred characteristic of this and other silica gels for use in the invention.

20 In one instance of the preparation of a catalyst for use in the invention three cubic feet (about 73 pounds) of the above described silica gel is covered with aqueous phosphoric acid having a concentration in the range 20 to 70%, but preferably about 55%, in which case 210 to 250 lbs may be used for the specified amount of silica gel. The preparation is allowed to stand, preferably for about 2 hours, after which time the excess aqueous phosphoric acid is drained off. The preparation is then air dried for 3 to 24 hours, preferably 10 to 15 hours, after which it is dried in the oven for 1 to 4 hours, preferably for 2 hours, at 100°—200°C, and preferably about 110°C. It may instead be preferred to dry in a stream of warm nitrogen gas. The whole operation may be conducted in situ, the silica gel support being placed in a reactor where it is impregnated with the phosphoric acid.

25 The phosphoric acid employed in forming the catalyst should preferably be a clear, clean, colourless, odourless, syrupy liquid meeting the requirements listed in the National Formulary XII Edition (NF XII) 1965, the Food Chemicals Codex, and the ACS** Reagent Chemicals, 1960 Edition for Phosphoric Acid:

Characteristics	Limits
Appearance	Water-white liquid with no visible foreign matter
Colour, APHA*	20 Maximum
Turbidity, APHA*	5 Maximum
Odour	No foreign odour
Total P_2O_5	61.56—62.28%
Total H_3PO_4	85.0—86.0%
Arsenic as As_2O_3	0.5 ppm Maximum
Fluorine as F	10.0 ppm Maximum
Heavy metals as Pb	10.0 ppm Maximum
Alkali phosphates	0.20% Maximum
Sulphates (SO_4)	0.003% Maximum
Nitrates (NO_3)	0.005% Maximum
Chloride (Cl)	0.003% Maximum
Reducing substance	To pass ACS** test
Volatile acids (as CH_3COOH)	0.0010% Maximum
Iron as Fe	0.003% Maximum
**American Chemical Society	*American Public Health Association

- Although the catalyst can be used for the hydration of various olefins, it is particularly effective when employed in the hydration of ethylene or other normally gaseous olefins such as propylene or butylene. Accordingly, the invention will be described hereinafter as it relates to the hydration of such gaseous olefins, and more particularly to the hydration of ethylene.
- Ethylene used as feed to the hydration should preferably be free of acetylene, since only a few parts per million of this impurity cause formation of the by-product cuprene ($C_{14}H_{16}Cu_2$) in the presence of even trace amounts of copper in raw materials or structural materials. Cuprene fouls the catalyst bed. Furthermore, acetylene is a precursor to crotonaldehyde, a deleterious by-product of hydration. Acetylene should preferably not be present in amounts greater than 30 parts per million, most preferably less than about 5 ppm. The ethylene feed should preferably be above 99% pure, but the process is operable with ethylene containing up to 15% inert gases such as ethane, propane, hydrogen, nitrogen, helium, argon, carbon dioxide and carbon monoxide.
- The mole ratio of water to ethylene in the feed should preferably be in the range 0.4:1.0 to 2.0:1.0, most preferably 0.5:1.0 to 0.8:1.0. The vapour velocity ($H_2O + C_2H_4$) should preferably be in the range of 20 to 60 standard cubic feet (at 60°F.) per minute per cubic foot of catalyst bed. The most preferred range, however, is 25 to 45 SCFM per cubic foot catalyst. The range of pressure should preferably be 500 to 1500 psi, most preferably 900 to 1250 psi. The range of temperature should preferably be 250° to 320°C., most preferably 265° to 300°C.
- In one embodiment, for the hydration of ethylene according to the invention, the impregnated catalyst is placed in a pressure vessel which is purged with inert gas, and then heated to hydration reaction temperature of about 300°C. A gaseous mixture of ethylene and water at reaction temperature and at reaction pressure near 1000 psi is continuously passed through the catalyst at a rate in the range of 25 to 40 SCFM per cubic foot of catalyst. The ethylene is thereby catalytically hydrated with water to yield ethanol. The effluent gases are cooled to condense the bulk of the ethanol. Uncondensed vapor consisting mostly of ethylene, but containing also ether and other compounds, is continuously recycled to the reactor after scrubbing with water to remove additional alcohol and after being joined by a make up stream of gaseous water and ethylene. The crude liquid alcohol together with scrubber water is initially purified by distillation, followed by catalytic hydrogenation to saturate aldehydes and unsaturates, and finally by a second distillation, all steps being operated continuously. Phosphoric acid is added to the catalyst as an aqueous solution to replace that lost by entrainment or by volatilization. Addition of the phosphoric acid may be on a continuous or intermittent basis. The silica gel used should be mechanically and chemically stable to aqueous solutions and long exposure to steam up to 320°C., and preferably at 300° to 320°C.
- Hydrogen gas used in hydrogenation of the alcohol product to remove unsaturates and reducing substances such as acetaldehyde, and crotonaldehyde, should be free of carbon monoxide since this is a hydrogenation catalyst poison. While the preferred purity of hydrogen gas is above 99%, the presence of inert gas up to 15% can be tolerated.
- Vapor phase hydration using the silica gel impregnated catalyst according to this invention can result in good conversion of ethylene

to alcohol and to ether as well as good space time yields of alcohol and ether in terms of gallons per cubic ft. catalyst per hour. The specific catalyst according to this invention is

5 equally useful in vapor phase hydration of other olefins to make the corresponding alcohols and ethers.

The use of the process according to the invention for vapor phase hydration of ethylene to ethanol can also provide good production rates of alcohol per unit of catalyst volume, without a sacrifice of the level of conversion of ethylene to ethanol relative to the equilibrium value. Thus, under conditions described in Example 1 given hereinbelow, in which a catalyst according to the invention was used, alcohol was produced at a rate of 1.06 gallons per cubic foot of catalyst per hour at a conversion level of 6.66% of the ethylene feed, or

20 89% of the equilibrium level of 7.47%.

Example 1.

A low density silica gel was selected as the phosphoric acid support for use in the preparation of an ethylene hydration catalyst. It had the following specific properties and characteristics:

	Pore volume (cc./gm.)	1.16
	Surface Area (sq.m./gm.)	325
	Average Pore Diameter (Å)	140
30	Total Volatile (Wt. %—1750°F.)	4.5
	Bulk Density (lb/cu.ft.)	27
	SiO ₂ (Wt. %—Dry Basis)	99.5
	Fe ₂ O ₃ (Wt. %—Dry Basis)	0.01
	Na ₂ O (Wt. %—Dry Basis)	0.06
35	Mesh Size (U.S. Standard)	6

To prepare the hydration catalyst, 500 ml of the above characterized silica gel support were immersed in 55 wt. % aqueous H₃PO₄ solution and allowed to stand 2 hours after which the preparation was drained and allowed to dry in air at a temperature of about 27°C. for 16 hours. The dried preparation was subjected to attrition by placing it in a vertical glass pipe 3/4 inch in diameter and 36 inches high and directing a jet of air through the column for an hour. It was then sieved, and particles larger than 8 mesh were retained as hydration catalyst. Analysis of the finished catalyst showed it to contain 41.5 wt. % non-bound orthophosphoric acid and to have a bulk density of 76 grams per 100 ml catalyst.

190 ml of the catalyst prepared as described above were charged to a jacketed 316 stainless steel vertical cylindrical reactor measuring 1—1/4 inches in diameter and 12—5/6 inches long. The liner of the reactor was made of "Hastelloy" (Trade Mark) B alloy, a nickel/molybdenum alloy in which nickel is the principal component.

60 The reactor, designed to operate at 1000 psi total pressure and 300°C., was closed at the top and at the bottom by means of 2 pairs

of grooved bolted flanges 4—1/2 inches in diameter and 1—1/4 inches thick with octagonal copper rings fitted to the grooves in the flanges to serve as gaskets.

A mixture of gaseous ethylene and water vapor at about 300°C. and having a mole ratio of water to ethylene of 0.74 was continuously passed downward through the catalyst bed at 298°C. at a vapor velocity of 26.3 standard cubic feet of reactants per minute per cubic foot of catalyst. The total pressure of the system was 1000 psi.

On continuous passing of ethylene through the catalyst bed, hydration of the ethylene to ethanol, ether and minor amounts of other oxygenated carbon compounds occurred as well as polymerization of the ethylene to minor amounts of various types of hydrocarbons.

The effluent vapors were partially condensed at 0°C. to -10°C. to yield an aqueous liquid product and the total effluent allowed to pass out of the system by means of a control valve into a receiver for the aqueous liquid product at atmospheric pressure. Non-condensed vapor in the effluent was dried, then further cooled at -78°C. to collect a vapor product of condensibles such as ether and other low boiling by-products, and finally residual effluent gas consisting principally of ethylene was vented.

Results of the test, based on gas-liquid chromatographic analysis for alcohol and ether, showed that over a test period of 21.8 hours of reaction, a conversion of ethylene to ethanol of 6.66%, and a conversion of ethylene to ether of 3.45% occurred. The production rate of alcohol and ether in terms of space time yields were 1.06 and 0.49 gallons per cubic foot of catalyst per hour.

Oil in the liquid product and in the vapor product was produced at rates of 0.016 and 0.162 pounds per cubic foot catalyst per hour, and H₃PO₄ was lost from the catalyst to the effluent liquid product at a rate of 0.01 pounds per cubic foot catalyst per hour.

The pH of the liquid product was 3.25, and the alcohol content was 17.79% by weight.

Example 2

This example illustrates the employment of the improved catalyst on a pilot plant scale under conditions conducive to a high production rate of alcohol.

The silica gel support used was equivalent to that used in Example 1.

The silica gel was screened to 1/8 to 3/16 inch particle size, then placed in a jacketed copper lined pressure vessel 11—1/8" internal diameter and 6' long. 2.9 Cubic feet of silica gel was used. The gel was soaked in situ for 3 hours with 55% aqueous H₃PO₄ at 75°F. The excess acid was then drained off, and the catalyst dried by passing nitrogen at 60°F. through the bed for 12 hours at a rate of 1150 lbs/hr/ft². The catalyst was further

dried by passing nitrogen at 210°F. through the bed for 8 hours until the bed temperature was 200°F. and then heated 2 more hours at 200°F.

- 5 Ethylene and steam were then passed downward through the bed in a mole ratio of water to ethylene of 0.53 at a vapor velocity of 43 SCFM/cu. ft. catalyst (60°F., 1 atm.) or reactants and at a total pressure of 1240 psi. The
10 inlet temperature was 516°F. and the outlet temperature was 543°F.

- The effluent vapors were neutralized, then cooled to 80—100°F. to condense liquid product. Non-condensed vapors consisting mainly
15 of ethylene were scrubbed with water in a packed tower for removal of alcohol, then recycled via a diaphragm compressor.

- Results of the run showed conversion of ethylene to alcohol to be 7.31% with an alcohol production rate in terms of space time
20 yield of 2.25 gallons alcohol per cubic foot catalyst per hour, which amounts to a substantially higher production level than shown in the known art.

- 25 WHAT WE CLAIM IS:—

1. A process for the preparation of an alkanol by olefin hydration which comprises reacting a gaseous mixture of an olefin and water at elevated temperature and pressure in the
30 presence of an olefin hydration catalyst which comprises a solid, porous silica gel support having a pore volume of from 1 to 2.2 cc per gram and a surface area from 200 to 600

square metres per gram, impregnated with phosphoric acid.

2. A process according to claim 1 wherein the silica gel support has a pore volume of from 1.0 to 1.2 cc/gram and a surface area of from 300 to 400 m²/gram.

3. A process according to claim 1 or 2 in which phosphoric acid is added to the system to replace that lost during reaction.

4. A process according to claim 1, 2 or 3 wherein ethylene is hydrated to form ethanol.

5. A process according to claim 4 wherein the mole ratio of water to ethylene is in the range 0.4:1 to 2.0:1 and the vapour velocity of water and ethylene is in the range 20 to 60 standard cubic feet (at 60°F) per minute per cubic foot of catalyst.

6. A process according to claim 4 or 5 wherein the pressure of operation is from 500 to 1500 psi.

7. A process according to claim 4, 5 or 6 wherein the reaction temperature is from 250 to 320°C.

8. A process for the preparation of ethanol substantially as hereinbefore described in any one of the Examples.

9. An alkanol prepared by a process according to any one of claims 1 to 8.

REDDIE & GROSE,
Agents for the Applicants,
6 Bream's Buildings,
London, EC4A 1HN.

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